

Extension of the Thermodynamic Perturbation Theory of Wertheim to Model Solid Phases of Attractive Chain Molecules

C. Vega

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, Madrid, Spain

F.J. Blas

Departamento de Física Aplicada Facultad de Ciencias Experimentales, Universidad de Huelva, Huelva, Spain

A. Galindo ^{C, S}

Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, London, United Kingdom

The first order perturbation theory (TPT1) of Wertheim has proved extremely successful in the modeling of fluid phases of hard chain-like molecules. In the context of the statistical associating fluid theory (SAFT), it has been shown to be also very effective in modeling the fluid phase behavior of chain-like molecules with attractive interactions, and it is now commonly used to model chain fluids of industrial interest. In this contribution we present a simple extension of the approach, which allows us to take into account solid as well as fluid phases of attractive chain molecules. In the implementation of the original TPT1 approach, the only information required to describe the properties of the chain fluid are the properties (the equation of state and structure) of a reference monomer fluid. It turns out that this statement is also true in the solid phase. In this way, we derive an equation of state phase suitable for fluid and solid phases of chain molecules. We present the global (solid-liquid-vapor) phase diagram of Lennard-Jones chain molecules of varying chain lengths, and compare our results with computer simulations. Excellent agreement is found in terms of the pressure, internal energy and free energy of the systems considered. In agreement with experimental data, asymptotic limits for the critical and triple temperatures are obtained as the chain length increases, although the inherent flexibility of the TPT1 model means that the calculated fluid range is greater than seen experimentally.